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(54) HIGH MOLECULAR WEIGHT MALEIC AND FUMARIC ACID ESTERS AND LUBRICANTS AND FUELS CONTAINING THE SAME

- (71) We, THE LUBRIZOL CORPORATION, a corporation organised and existing under the laws of the State of Ohio, United States of America, of Box 3057 Euclid Station, Cleveland, Ohio 44117, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention is concerned with novel esters of certain substituted maleic and fumaric acids with monohydric and polyhydric alcohols as well as lubricants and fuels containing these esters.
- According to the invention there is provided an oil-soluble ester of a substituted maleic or fumaric acid wherein the substituent is substantially aliphatic, substantially saturated and substantially hydrocarbon, as hereinafter defined, and contains at least thirty aliphatic carbon atoms, and a monohydric or polyhydric alcohol. Preferably the ester is an ester of a poly(1-monoolefin)-substituted maleic acid or fumaric acid wherein the poly(1-monoolefin) substituent has at least fifty aliphatic carbon atoms and a mono- or polyhydric alkanol of up to twelve carbon atoms. Desirably the polyhydric alkanol contains 3 to 6 hydroxyl groups and up to six carbon atoms.
- Throughout the specification and claims, the expression "substantially aliphatic, substantially saturated and substantially hydrocarbon" as applied to the substituent of the maleic or fumaric acid, means that the substituent may contain olefinic linkages, aryl groups and polar substituents but only in amounts insufficient to alter its generally aliphatic, saturated and hydrocarbon nature.
- Generally, the substituents will be aliphatic hydrocarbon substituents having an average molecular weight of about 400 to about 10,000 and preferably from about 700 to about 5,000. These substituted maleic and fumaric acid acylating agents are readily prepared by reacting an ethylenically unsaturated reactant containing at least thirty aliphatic carbon atoms with bromo- or chloro-substituted maleic or fumaric acid compounds such as the 2-chloro, 2-bromo, 2,3-dichloro, or 2,3-dibromo-derivatives of maleic acid anhydride, maleic acid mono-C₁—C₇ alkyl ester, maleic acid di-C₁—C₇ alkyl ester, maleic acid monochloride, maleic acid dichloride, fumaric acid, mono-C₁—C₇ alkyl fumaric acid ester, di-C₁—C₇ alkyl fumaric acid ester, monochloride of fumaric acid, or the dichloride of fumaric acid. The resulting products are the corresponding substituted maleic or fumaric acid acylating agent.
- The ethylenically unsaturated reactant used in the preparation of the substituted maleic and fumaric acid acylating agents are principally the high molecular weight, ethylenically unsaturated petroleum fractions and substantially saturated olefin polymers. The olefin polymers derived from monoolefins (i.e., poly(1-monoolefins)) having from two to thirty carbon atoms are preferred reactants. The especially useful polymers are the polymers of 1-monoolefins such as ethylene, propene, 1-butene, isobutene, 1-hexene, 1-octene, 2-methyl-1-heptene, 3-cyclohexyl-1-butene, 2-methyl-5-propyl-1-hexene. Polymers of medial olefins, i.e., olefins in which the olefinic linkage is not at the terminal position, likewise are useful. These are exemplified by 2-butene, 3-pentene, and 4-octene.
- The interpolymers of 1-monoolefins such as illustrated above with each other and with other interpolymers of olefinic substances such as aromatic olefins, cyclic olefins, and polyolefins, are also useful sources of the ethylenically unsaturated reactant. Such interpolymers include, for example,

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those prepared by polymerizing isobutene with styrene, isobutene with butadiene, propene with isoprene, propene with isobutene, ethylene with piperylene, isobutene with chloroprene, isobutene with p-methoxystyrene, 1-hexene with 1,3-hexadiene, 1-octene with 1-hexene, 1-heptene with 1-pentene, 3-methyl-1-butene with 1-octene, 3,3-dimethyl-1-pentene with 1-hexene and isobutene with styrene and piperylene.

For reasons of oil-solubility and stability, the interpolymers contemplated for use in preparing acylating agents are substantially aliphatic and substantially saturated, that is, they will normally contain at least 80% and preferably 95% on a weight basis of units derived from aliphatic monoolefins. Preferably they will contain no more than 5% olefinic linkages based on the total number of the carbon-to-carbon covalent linkages present. Any pendant aryl groups such as would result from the use of styrene as an interpolymizable monomer will normally not exceed one such pendant aryl group per average of twenty-five aliphatic carbon atoms in the substituent. Preferably, the substituents will be completely aliphatic. Usually, the ethylenically unsaturated aliphatic reactant will be an ethylenically unsaturated, aliphatic hydrocarbon reactant but ethylenically unsaturated, aliphatic, substantially hydrocarbon reactants containing polar substituents are also contemplated. Such polar substituents include hydroxy, mercapto, nitro, oxo, thio, and the like. Polar substituents, if present, will not normally exceed 10% by weight of the total weight of the hydrocarbon portion of the ethylenically unsaturated aliphatic reactant.

The ethylenically unsaturated reactants used in the preparation of the acylating agents normally have molecular weights of from 400 up to 10,000, preferably about 700—5,000. The preferred reactants are the above described poly(1-monoolefins) having an average molecular weight of 700 to 5,000. When however, the acylating agent is derived from a polyolefin having an average molecular weight in excess of about 10,000, the esters prepared therefrom also possess viscosity index improving capabilities in addition to their sludge-dispersing capabilities. Especially preferred reactants are polyisobutylene, polypropylene, polyethylene, and ethylene-propylene copolymers having average molecular weights of 700 to 5,000. Polyisobutylene is the single most preferred ethylenically unsaturated poly(1-monoolefin) reactant.

To prepare the substituted maleic or fumaric acid acylating agent, all that is required is that the ethylenically unsaturated reactant as described above be intimately admixed with one of the above identified chloro- or bromo-substituted maleic or

fumaric acid compounds and heated at a temperature usually within the range of 200°—300°C., preferably from 230°—260°C. Usually, the ethylenically unsaturated reactant and the monochloro- or monobromo-substituted maleic or fumaric acid compounds are mixed in a mole ratio of 1:1 to 1:1.5. If the ethylenically unsaturated reactant contains more than one ethylenic linkage and if it is desired to incorporate an average of more than one maleic or fumaric acid group per hydrocarbon molecule, the 1—1.5 moles or more of the monochloro- or monobromo-substituted maleic or fumaric acid compound can be employed per ethylenic linkage. Similarly, acylating agents having an average of more than one substituent per maleic or fumaric group can be prepared by reacting the ethylenically unsaturated reactant with dichloro- or dibromo-substituted maleic or fumaric compounds as identified hereinbefore in mole ratios of unsaturated reactant to maleic or fumaric acid compound of 1.1:1 to 2.5:1. Up to two substituents per maleic or fumaric acid groups can be formed in this manner.

This reaction can be conducted in the presence of an inert liquid diluent although diluents normally are not necessary. Suitable diluents include the aliphatic, aromatic, and cycloaliphatic hydrocarbons and chlorinated hydrocarbons such as benzene, toluene, xylene, chlorobenzene, heptane, decane, cyclohexane, and the like. Other conventional diluents can be employed such as Stoddard Solvent, and the like. Due to the reaction temperature, the use of diluents having boiling points less than the preferred reaction temperatures generally results in an unnecessary increase of the reaction time. Thus, if a diluent is utilized, it will generally be a high boiling diluent such as a low viscosity mineral oil.

As the substituted maleic acids, substituted maleic acid anhydrides, and substituted fumaric acids are the preferred acylating agents for preparing the esters of this invention, chloro-substituted maleic acid, chloro-substituted maleic acid anhydride, and chloro-substituted fumaric acid are generally utilized in preparing the acylating agents.

The esters are generally prepared by reacting the substituted maleic or fumaric acid acylating agents with the desired alcohol according to conventional esterification procedures. The alcohol reactant can be either a mono- or polyhydric alcohol and can be quite diverse in structure and chemical composition. Ordinarily, these alcohol reactants will contain not more than forty aliphatic carbon atoms but in the case of polyoxyalkylene alcohols, they may contain more carbon atoms. A preferred group of

alcohol reactants are the mono- and polyhydric C_1-C_{12} alkanols.

Monohydric alcohols include 1-butanol, 1-decanol, 1-hexadecanol, 2-butene-1-ol, 1-hentriacontanol, 2-ethyl-1-butanol, 2-ethyl-1-hexanol, lauryl alcohol, stearyl alcohol, tert-butyl alcohol, amyl alcohols, cyclohexanol, 2-cyclohexylethanol, N,N-diethylethanolamine, 2-phenylethanol, and the monoaryl ethers, monoalkyl ethers, and monoaralkyl ethers of alkylene glycols such as the monoethyl ether of ethylene glycol, the monophenyl ether of propylene glycol, and the monophenethyl ether of tetramethylene glycol.

Useful polyhydric alcohols include alkylene glycols and polyoxyalkylene glycols such as ethylene glycol, propylene glycol, trimethylene glycol, butylene glycol, and polyglycols such as diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, tripropylene glycol, dibutylene glycol, tributylene glycol, and other alkylene glycols and polyoxyalkylene glycols in which the alkylene radical contains from two to eight carbon atoms. These include the reaction products of various polyhydric alkanols such as pentaerythritol, trimethylol-ethane, trimethylolpropane, glycerol, mannitol with alkylene oxides such as ethylene oxide, propylene oxide, butylene oxide, mixtures of these, or sequential reactions involving first one and then the other to produce, for example, polyoxyalkylene triols and tetrols having average molecular weights of 800 to 5000. The monoethers of the polyoxyalkylene glycols are also useful in preparing esters of the present invention. These include the monoaryl ethers, monoalkyl ethers, and monoaralkyl ethers of the formula $HO-(R_1-O)_n-R_2-OR_3$ where R_1 is aryl such as phenyl, C_1-C_7 alkoxy phenyl, and C_1-C_7 alkyl phenyl; R_2 is alkyl such as ethyl, propyl, tert-butyl and pentyl; and aralkyl such as benzyl, phenylethyl, phenylpropyl and p-ethylphenylethyl; n is a whole number of 2 to 150, and R_1 and R_2 are lower alkylene of up to eight, preferably, two to four carbon atoms.

Other useful polyhydric alcohols include glycerol, monomethyl ether of glycerol, pentaerythritol, 9,10-dihydroxystearic acid, the ethyl ester of 9,10-dihydroxystearic acid, 3-chloro-1,2-propanediol, 1,2-butanediol, 1,4-butanediol, 2,3-hexanediol, 2,4-hexanediol, pinacol, erythritol, arabitol, sorbitol, mannitol, 1,2-cyclohexanediol, 1,4-cyclohexanediol, 1,4-(2-hydroxyethyl)-cyclohexane, 1,4-dihydroxy-2-nitro-butane, 1,4-di(2-hydroxyethyl)-benzene, the carbohydrates such as glucose, mannose, mannose, glyceraldehyde, and galactose, di(2-hydroxyethyl)amine, tri(3-hydroxypropyl)amine, N,N'-di(hydroxyethyl)-ethylenediamine and copolymer of

allyl alcohol and styrene. Alkylene oxides containing up to ten aliphatic carbon atoms are also useful for reacting with the substituted maleic and fumaric acids to prepare esters of this invention. Suitable alkylene oxides include ethylene oxide, propylene oxide, 1,2-butylene oxide, styrene oxide, and the like.

Included within this group of aliphatic alcohols are those polyhydric alcohols containing at least three hydroxyl groups, at least one of which has been esterified with a monocarboxylic acid having from eight to thirty carbon atoms such as octanoic acid, oleic acid, stearic acid, linoleic acid, dodecanoic acid, or tall oil acid. Examples of such partially esterified polyhydric alcohols are the monooleate of sorbitol, sorbitan monooleate, the monooleate of glycerol, the monostearate of glycerol, the distearate of sorbitol, and the di-dodecanoate of erythritol.

A preferred class of esters are those prepared from polyhydric alcohols containing up to ten carbon atoms, and especially those containing three to ten carbon atoms. This class of alcohols includes glycerol; erythritol, pentaerythritol, dipentaerythritol, gluconic acid, glyceraldehyde, glucose, arabinose, 1,7-heptanediol, 2,4-heptanediol, 1,2,3-hexanetriol, 1,2,4-hexanetriol, 1,2,5-hexanetriol, 2,3,4-hexanetriol, 1,2,3-butanetriol, 1,2,4-butanetriol, quinic acid, 2,2,6,6-tetrakis(hydroxymethyl)-cyclohexanol, 1,10-decanediol, digitalose, and the like. The esters prepared from aliphatic alcohols containing at least three hydroxyl groups and up to ten carbon atoms are particularly preferred.

An especially preferred class of polyhydric alcohols for preparing the esters of the present invention are the polyhydric alkanols containing three to ten carbon atoms and, particularly, those containing three to six carbon atoms and having at least three hydroxyl groups. Such alcohols are exemplified in the above specifically identified alkanols and are represented by glycerol, erythritol, pentaerythritol, mannitol, sorbitol, 1,2,4-hexanetriol, trimethylolpropane, trimethylolpropane, and the like.

Amino alcohols are also contemplated as being suitable for preparing the esters and may be monohydric or polyhydric amino alcohols. Examples are the N-hydroxy C_1-C_7 alkyl amines and polyamines such as 2-hydroxyethylamine, 3-hydroxybutylamine, di-(2-hydroxyethyl)amine, tri-(2-hydroxyethyl)amine, di-(2-hydroxypropyl)amine, N,N,N'-tri-(2-hydroxyethyl)ethylenediamine, N,N,N',N'-tetra-(2-hydroxyethyl)-ethylenediamine, N-(2-hydroxyethyl)-piperazine, N,N'-di-(3-hydroxypropyl)piperazine, N-(2-hydroxyethyl)morpholine, N-(2-hydroxyethyl)-2-morpholinone, N-(2-hydroxyethyl)-3-methyl-2-morpholinone, N-(2-hydroxypropyl)-6-methyl-2-

morpholinone, N-(2-hydroxyethyl)-5-carboethoxy-2-piperidone, N-(2-hydroxypropyl)-5-carboethoxy-2-piperidone, N-(2-hydroxyethyl)-5-(N-butylcarbonyl)-2-piperidone, N-(2-hydroxyethyl)piperidine, N-(4-hydroxybutyl)piperidine, N,N-di-(2-hydroxyethyl)glycine, and esters thereof with aliphatic alcohols, especially C₁-C₄ alkanols, N,N-di-(3-hydroxypropyl)glycine, and the like. Also contemplated are other mono- and poly-N-hydroxyalkyl-substituted alkylene polyamines wherein the alkylene radicals contain two to four carbon atoms and the polyamine has up to seven amino groups.

As mentioned above, the esters are prepared through conventional esterification techniques such as mixing the alcohol and carboxylic acid acylating agent and heating the mixture at a temperature of at least 100°C. up to the decomposition temperature and usually at 150°-300°C. The reaction may be conducted in the presence of a substantially inert liquid diluent and known esterification catalyst. Suitable diluents include the aliphatic, cycloaliphatic, and aromatic hydrocarbons and their chlorinated analogs exemplified by hexane, heptane, cyclohexane, benzene, toluene, xylene, chlorobenzene, chlorohexanes, and the like. Mineral oils, naphthas, ligroin, and the like may also be used as a diluent.

The reaction mixture comprises at least one of the above-described substituted maleic or fumaric carboxylic acid acylating agents and at least one of the foregoing types of alcohols. The esterification products contemplated by the present invention include mixtures of esters prepared by reacting one or more different acylating agents with one or more different alcohols of the general type described hereinabove. Similarly, ester mixtures suitable as lubricant and fuel additives can be prepared by mixing two or more separately prepared esters.

It is also contemplated that the esterification products of this invention may be contacted with organic or inorganic bases to neutralize any acidity in the esterification product. Alkaline earth metal bases such as calcium oxide, calcium hydroxide, barium oxide, barium hydroxide, and barium ethoxide are suitable inorganic bases. Amines such as ethylamine, propylamine, diethylamine and tetraethylene pentamine, are suitable organic bases. It is not necessary that any residual acidity be neutralized, however, since the esterification products are useful dispersants without neutralization. Indeed in most instances there is little, if any residual acidity where sufficient alcohol is employed to react with all the carboxyl groups.

Usually, at least one equivalent of alcohol is employed for each mole of acylating agent. Normally, there is no advantage in using more than about one mole of alcohol for

each equivalent of acid acylating agent. The acylating agents have one equivalent per carboxyl group or equivalent derivative (e.g.,

$\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{Cl} \end{array}$ while the number of equivalents in an alcohol per mole depends upon the number of free alcoholic hydroxy groups present therein. Accordingly, if there is one maleic or fumaric acid group per substituted maleic or fumaric acid acylating agent, the acylating agent has two equivalents per mole. Similarly, glycerol has three equivalents per mole; pentaerythritol, four; tri-(2-hydroxyethyl)amine, three; and polyoxyethylene glycol, two. Ordinarily, the total amount of acylating agent and alcohol used in the reaction mixture will vary from a ratio of 1:1 equivalents to 1:1 mole.

As will be apparent to those skilled in the art, the esterification product may be an acidic ester or diester or a mixture thereof. Especially where the alcohol reactant is a polyhydric alcohol, the esterification product is likely to be a mixture of various complex esters.

The following examples illustrate preferred embodiments of this invention. As used in these examples and elsewhere in the specification and claims, "percentage," and "parts" refer to percent by weight and parts by weight unless otherwise indicated.

EXAMPLE 1

(a) A mixture consisting of 5000 parts of polyisobutylene having an average molecular weight of about 1000 and 660 parts of chloromaleic acid anhydride is heated to reflux (about 200°C.) with nitrogen blowing over a one-hour period. With continued heating the temperature rises to about 240°C in four hours. The mixture is maintained at 240°-245°C. for five hours, cooled to 210°C., stripped to a temperature of 215°C. at 30 mm(Hg), and filtered. The filtrate is the desired polyisobutenyl-substituted maleic acid anhydride. It has a neutralization number (phenolphthalein) of 60 (acid).

(b) The general procedure of (a) is repeated using 660 parts of chlorofumaric acid to produce the corresponding polyisobutenyl-substituted fumaric acid.

(c) The general procedure of (a) is repeated using 400 parts of 2,3-dichloromaleic acid to produce the corresponding dipolyisobutenyl-substituted maleic acid acylating agent.

By substituting other ethylenically unsaturated reactants of the type described hereinbefore for the polyisobutylene or by using other chloro- or bromo-substituted maleic or fumaric acid compounds as described hereinbefore, in lieu of the chloromaleic acid anhydride, chlorofumaric, or 2,3-dichloromaleic acid, other substituted

maleic and fumaric acid acylating agents can be prepared.

EXAMPLE 2

- 5 (a) A mixture comprising 2910 parts of the substituted maleic acid anhydride prepared according to the process of Example 1(a) and 351 parts of pentaerythritol are heated with nitrogen blowing at a temperature maintained within the range of about 200°—216°C. for five and one-half hours. Then, 7 parts of imidazole is added to the mixture which is then held at a temperature of about 208°—213°C. for about 2.25 hours while continuing the nitrogen blowing. Then 15 an additional 10 parts imidazole are added and the mixture is maintained at 198°—216°C. for 5.5 hours. Infrared analysis of the esterification mixture at this point shows the presence of some unreacted anhydride. 20 A mixture comprising 140 parts dimethyl formamide and 40 parts xylene is added to the esterification product which is then heated at 196°—212°C. to remove substantially all water in the esterification product. 25 At that point the temperature is slowly raised to 225°C. and maintained at 225°—228°C. with nitrogen blowing to remove the xylene. The product is the desired pentaerythritol ester of polyisobutenyl-substituted maleic acid. 30 (b) To the esterification product of 2(a) there is added fifty parts of a commercial ethylene polyamine mixture having an average composition corresponding to that of pentaethylene hexamine over a 0.25 hour period while maintaining a temperature of 35

about 225°C. Then, 2630 parts of low viscosity mineral oil added over a one-hour period during which time the mixture cools to about 155°C. The resulting product is filtered at a temperature of 130°—135°C. 40 The filtrate is a 44.7% by weight oil solution of the desired ethylene polyamine-treated esterification product. It has a nitrogen content of about 0.4%, and OH content of about 1.45% by weight and a neutralization number (phenolphthalein) of 1.9 (acid). 45

EXAMPLE 3

A reaction mixture comprising 2250 parts of polyisobutenyl-substituted fumaric acid produced according to the general procedure of Example 1(b) having an average molecular weight of about 1100 and about 91 parts of sorbitol is reacted at a temperature of about 140°—160°C. in the presence of 12 parts of p-toluene sulfonic acid, 500 parts xylene, and 500 parts mineral oil. During the heating phase, water is removed as an azeotrope with xylene. After water evolution substantially ceases, the esterification product is filtered and then stripped to a temperature of 150°C. and a pressure of 20 mm(Hg). The stripped material is an oil solution of the desired polyisobutenyl-substituted fumaric acid esters of sorbitol. 55 60 65

Following the general procedure of Example 3, other esters of the type contemplated by this invention can be produced by reacting the following substituted maleic and fumaric acid acylating agents with the alcohols shown in the molar ratios indicated. 70

TABLE 1

	Acylating Agent (A)	Alcohol (B)	Molar Ratio (A):(B)
5	EXAMPLE 4 I*	Trimethylolpropane	1:1.5
	EXAMPLE 5 I*	Pentaerythritol	1:1
	EXAMPLE 6 I*	Sorbitol	1:0.75
10	EXAMPLE 7 Prod. of Ex. 1(c)	Triethanolamine	1:2
	EXAMPLE 8 II*	Polyethylene Glycol (Avg. Mol. Wt. 800—900)	1:2
15	EXAMPLE 9 I*	Tert-Butyl Alcohol	1:2.1
	EXAMPLE 10 II*	Propylene Oxide	1:2.5
20	EXAMPLE 11 I*	Pentaerythritol and Trimethylolethane (Equimolar Mixture)	***
25	EXAMPLE 12 I*	Monobutyl Ether of Diethylene Glycol	1:2.2
*Polyisobutenyl-substituted maleic acid anhydride having an average molecular weight of about 1450.			
**Polyisobutenyl-substituted fumaric acid having an average molecular weight of about 2500.			
30	***Equivalent ratio of (A) to (B) of 1:2.		

By selecting other substituted maleic acid and fumaric acid acylating agents such as those described hereinabove and other mono- or polyhydric alcohols and reacting them according to conventional esterification procedures, still other high molecular weight carboxylic acid esters of the type contemplated by this invention can be prepared.

As mentioned before, the high molecular weight, oil-soluble esters of this invention are useful as additives in lubricants and fuels. When employed as lubricating oil additives they can be present in amounts of from 0.01% to 30%, by weight in the final lubricating composition. Ordinarily, when used as additives for lubricating oil compositions, the esters will be present in amounts of from 0.1% to 10%, usually 0.5% to 5%, by weight although under unusually adverse

conditions, such as in the operation of certain marine diesels, they may comprise up to about 30% by weight of the lubricant. The esters are particularly useful as dispersants in lubricating oil compositions used in the crankcase of various internal combustion engines. Although they can be used effectively in gear and transmission lubricants, hydraulic fluids, greases, and the like. When employed in lubricating oils, the esters may be used alone or in combination with other dispersants or detergents. In addition, the lubricating composition may contain other conventional additives such as rust inhibitors, oxidation inhibitors, viscosity index improving agents, extreme pressure additives, and other ash-producing and/or ashless dispersants, and the like.

The esters of this invention can be effec-

tively employed in a variety of lubricating compositions based on natural or synthetic lubricating oils. The lubricating compositions contemplated are principally lubricating oils for both spark-ignition and compression-ignition internal combustion engines. However, other lubricating compositions can benefit from the incorporation of these additives including lubricants from automatic transmissions, gear lubricants, metal-working lubricants, and hydraulic fluids. While the above lubricating compositions are normally liquids, it is also anticipated that they may be converted to "thickened" lubricants or greases for specific applications by application of conventional grease-forming procedures without departing from the scope of this invention.

Natural oils include castor oil, lard oil, and solvent-refined or acid-refined mineral lubricating oils of the paraffinic, naphthenic, or mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful base oils. Other synthetic lubricating oils include hydrocarbon oils such as polymerized olefins (e.g., polybutylenes and polypropylenes); alkyl benzenes (e.g., dodecyl benzenes, tetradecyl benzenes, dinonyl benzenes and di-(2-ethylhexyl) benzenes); polyphenyls (e.g., biphenyls and terphenyls); and the like. Alkylene oxide polymers and derivatives thereof where the terminal hydroxyl groups have been modified by, for example, esterification or etherification, constitute another class of known synthetic lubricating oils. These are exemplified by the oils prepared through polymerization of propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methylpolyisopropylene ether having an average molecular weight of 1000, diphenylether of polyethylene glycol having a molecular weight of 500—1000 and diethylether of polypropylene glycol having a molecular weight of 1000—1500) or the C_1 — C_7 alkanoyl esters thereof such as the acetic esters. Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acids, succinic acid, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid and adipic acid) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol and 2-ethylhexyl alcohol). Specific examples of these esters include dibutyl adipate, di-(2-ethylhexyl)sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, dioctylphthalate, didecyl phthalate, dieicosyl sebacate, and the like. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate and the diethyl ester of decane phosphonic acid); alkyl diphenyl ethers; and polymerized tetrahydrofuranes. Silicone-based oils such as the polyalkyl-, polyaryl-,

polyalkoxy-, and polyaryloxy-siloxane oils and silicate oils comprise another useful class of synthetic lubricants (e.g., tetraethyl silicate, tetraisopropyl silicate, tetra-2-ethylhexyl silicate, tetra(4-methyl-2-tetraethyl) silicate, tetra-p-tert-butylphenyl silicate, hexyl-(4-methyl-2-pentoxo)disiloxane, poly(methyl)-siloxanes and poly(methylphenyl)-siloxanes). This identification of certain oils is not intended to be inclusive but is merely illustrative of the type of base oils contemplated by this invention.

In fuels, the esters promote engine cleanliness by reducing or eliminating harmful deposits in the fuel system. Their presence promotes carburettor and fuel line cleanliness and often reduces or eliminates the depositions of carbonaceous deposits in internal parts of the engine such as on exhaust parts. Normally, the esters used in fuels will be derived from acids having an average molecular weight of 400—2500 and alcohols containing not more than ten carbon atoms. The esters are primarily intended for use in the normally liquid petroleum distillate fuels, that is, the petroleum distillates which boil in the range characteristic of petroleum fuels such as gasolines, fuel oils, diesel fuels, aviation fuels, kerosene, and the like. When employed in fuels, they are generally employed in lower concentrations than in lubricants, for example, in amounts of from 0.0001% to 1% by weight and generally in amounts of from 0.001% to 0.1% by weight. As in the case of lubricants, other conventional additives can be present in the fuel compositions contemplated by the present invention. Additional additives include lead scavengers, decisers, antiscreen clogging agents, demulsifiers, smoke suppressants and the like.

The following are examples of the lubricating and fuel compositions contemplated by the present invention.

EXAMPLE A

SAE 30 mineral oil containing 1% of the products of Example 11 and 0.5% of the product of Example 2(a).

EXAMPLE B

SAE 20 mineral oil containing 0.75% of the product of Example 2(b) and 0.15% of the zinc salt of an equimolar mixture of di-cyclohexylphosphorodithioic acid and diisobutylphosphorodithioic acid.

EXAMPLE C

SAE 10W—40 mineral lubricating oil containing 1.5% of the product of Example 8, 0.075% of phosphorus as the adduct obtained by heating di-nonylphosphorodithioate with 0.25 mole of 1,2-hexene oxide at 100°C., a sulfurized methyl ester of tall oil acid having a sulfur content of 15%, 6%

of a polyisobutene viscosity index improver having an average molecular weight of about 80,000—100,000, 0.005% of poly-(alkylmethacrylate) anti-foam agent, and 0.5% lard oil.

EXAMPLE D

SAE 20 mineral lubricating oil containing 2.5% of the product of Example 7, 0.75% of phosphorus as the dioctylphosphorodithioate, 2% of a barium detergent prepared by neutralizing with barium hydroxide a hydrolyzed reaction product of a polypropylene (molecular weight 2000) with one mole of phosphorus pentasulfide and one mole of sulfur, 3% of a barium sulfonate detergent prepared by carbonating a mineral oil solution of mahogany acid and a 5% stoichiometrically excess amount of barium hydroxide in the presence of octylphenol as the promoter at 180°C., 3% of a supplemental ashless dispersant prepared by copolymerizing a mixture of 95% by weight of decylmethacrylate, 5% by weight of diethylaminoethyl acrylate.

EXAMPLE E

A di-2-ethylhexyl sebacate lubricating composition comprising 0.75% of the product of Example 9.

EXAMPLE F

Diesel fuel containing 0.02% of the product of Example 5.

EXAMPLE G

Gasoline containing 0.007% of the product of Example 5.

The foregoing compositions illustrate types of compositions contemplated by the present invention. Many additional compositions apparent to those skilled in the art are available simply by replacing all or part of the esters used in these fuels and lubricants with an equal amount of other esters of the present invention. Optimum amounts for any application will depend upon the particular additive or additive combination selected, the specific fuel or lubricant, and the specific environment in which the fuel or lubricant is to be used. These optimum amounts can be ascertained through conventional evaluation techniques commonplace in the industry.

WHAT WE CLAIM IS:—

1. An oil-soluble ester of a substituted maleic or fumaric acid wherein the substituent is substantially aliphatic, substantially saturated and substantially hydrocarbon, as hereinbefore defined, and contains at least thirty aliphatic carbon atoms, and a monohydric or polyhydric alcohol.

2. An oil-soluble ester according to Claim 1 wherein the substituent is an ali-

phatic hydrocarbon substituent having an average molecular weight of from 400 to 10,000.

3. An oil-soluble ester according to Claim 1 or 2 wherein the alcohol is a polyoxyalkylene alcohol.

4. An oil-soluble ester according to Claim 1 or 2 wherein the alcohol is a mono- or polyhydric alkanol of up to twelve carbon atoms.

5. An oil-soluble ester according to any preceding Claim wherein the ester is an acidic ester or a diester.

6. An oil-soluble ester according to Claim 1 or 2 which is an ester of a poly(1-monoolefin)-substituted maleic acid or fumaric acid wherein the poly(1-monoolefin) substituent has at least fifty aliphatic carbon atoms and a mono- or polyhydric alkanol of up to twelve carbon atoms.

7. An oil-soluble ester according to Claim 6 wherein the poly(1-monoolefin) substituent is derived from polyisobutylene, polypropylene, polyethylene, or an ethylene-propylene copolymer having an average molecular weight of from 700 to 5000.

8. An oil-soluble ester according to Claim 6 or 7 wherein the polyhydric alkanol contains 3 to 6 hydroxyl groups and up to six carbon atoms.

9. An oil-soluble ester according to any one of Claims 6 to 8 which is an ester of a poly(1-monoolefin)-substituted maleic acid.

10. An oil-soluble ester according to any one of Claims 6 to 9 which is an acidic ester or a diester.

11. An oil-soluble ester according to any one of Claims 6 to 10 which is an ester of trimethylol ethane, trimethylol propane, pentaerythritol, sorbitol, or mannitol.

12. An oil-soluble ester according to Claim 11 which is an ester of a polyisobutenyl-substituted maleic acid.

13. An oil-soluble ester according to Claim 12 which is an ester of pentaerythritol.

14. A lubricant or fuel composition comprising, respectively, a major amount by weight of a lubricating oil or normally liquid fuel and a minor amount by weight of at least one ester according to Claim 1.

15. A lubricant or fuel composition comprising, respectively, a major amount by weight of a lubricating oil or normally liquid fuel and a minor amount by weight of at least one ester according to Claim 3.

16. A lubricant or fuel composition comprising, respectively, a major amount by weight of a lubricating oil or normally liquid fuel and a minor amount by weight of an ester according to Claim 6.

17. A lubricant or fuel composition comprising, respectively, a major amount by weight of lubricating oil or normally liquid fuel and a minor amount by weight of an ester according to Claim 7.

18. A lubricant or fuel composition comprising, respectively, a major amount by weight of lubricating oil or normally liquid fuel and a minor amount by weight of an ester according to Claim 10. 5
19. A lubricant or fuel composition comprising, respectively, a major amount by weight of lubricating oil or normally liquid fuel and a minor amount by weight of an ester according to Claim 11. 10
20. A lubricant or fuel composition comprising, respectively, a major amount by weight of lubricating oil or normally liquid fuel and a minor amount by weight of an ester according to Claim 12. 15
21. A lubricant or fuel composition comprising, respectively, a major amount by weight of lubricating oil or normally liquid fuel and a minor amount by weight of an ester according to any one of claims 2, 4, 5, 8, 9 and 13. 20
22. A lubricant or fuel composition according to claim 14 substantially as hereinbefore described with reference to any one of Examples A to G. 25

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